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## **Report Title**

Microsphere Composites of Nano-Al and Nanothermite: An Approach to Better Utilization of Nanomaterials

### **ABSTRACT**

With the recent implementation of nano sized metal powders into energetic composites such as solid rocket propellants, incorporating metal nanoparticles with high mass loading in the propellant has become an issue. In this work, an electrospray deposition technique was employed to increase particle loading of nano aluminum (n-Al) and demonstrate the potential of the fluoropolymer, polyvinylidene fluoride (PVDF), as an energetic binder. A mass percentage of 50 % n-Al in PVDF was determined to have the optimal combustion qualities when ignited in air. The Al/PVDF energetic nanocomposite film morphologies were analyzed using scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). Combustion characteristics of the film were analyzed using thermogravimetric analysis/mass spectrometry (TGA/MS) and temperature jump time of flight mass spectrometry (T-jump TOFMS). Ignition temperatures were determined at various pressures in air and argon environments.

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# Microspheres Composite of Nano-Al and Nanothermite: An Approach to Better Utilization of Nanomaterials

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Nanometallic fuels suffer from processing challenges that have significantly retarded their utility, primarily because their very high surface area/small particle size increases the viscosity of the polymer binder and oxidizer mix, such that high mass fractions of fuel cannot be formulated. The other concern is that they lose surface area rapidly, on a time-scale commensurate with combustion. We employ electrospray as a means to create a gel within a droplet by evaporation induced rapid aggregation of aluminum and oxidizer nanoparticles containing a small mass fraction of an energetic binder. We find that the average size of the microparticles can be systematically changed from 2  $\mu\text{m}$  to 16  $\mu\text{m}$ . The combustion behavior is found to be very different from either nanoaluminum or micron aluminum and their corresponding thermite mixtures. The material which is super-micron sized has surface area consistent with the nanoparticle comprising it and the binder serves to act as a gas generator to minimize sintering.

## I. Introduction

Due to its high enthalpy and ready availability, conventional aluminum powders with an average size of 3-20  $\mu\text{m}$ , are commonly employed in solid rocket propellant and other propulsive systems.<sup>1-15</sup> Although the energy density is increased after incorporation of micrometer-sized aluminum fuel in propellant systems, the burning rate however was not found to improve much, resulting in low rates of energy release.<sup>16</sup> Additionally, the oxide coating on the surface of microsized aluminum sufficiently passivates the fuel to a high ignition temperature  $\sim 2300\text{ K}$ .<sup>2, 4, 17</sup> In contrast, the use of nanoscale aluminum lowers the ignition temperature to  $< 1000\text{ K}$ , with a much enhanced burning rate and a lower ignition delay time.<sup>17-23</sup>

Unfortunately nanometallic fuels suffer from two significant problems:<sup>20, 24-27</sup>

1. Processing challenges that have significantly retarded their utility, most primarily because their very high surface area/small particle size increases the viscosity of polymer binder and oxidizer mix, such that high mass fractions of fuel cannot be formulated.
2. Evidence points to the rapid loss of surface area of nanomaterials, which serves to lead to a fractional power dependence in burning rate with respect to diameter. i.e.  $d^{0.3-0.5}$ .

In this paper we describe a strategy to mitigate the above issues. We demonstrate the formation of mesoparticles comprising nanoparticles of aluminum as the fuel, a gas generator (Nitrocellulose), and in some cases copper oxide as an oxygen carrier.

1. The function of the microparticle is to create a structure whose dimensions should make it easier to process, but still contain an accessible surface area commensurate with nanostructures.

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2. The function of the gas generator is to enhance burning and to promote separation of particles from one another to delay the onset of sintering and thus preserve active surface area for as long as possible.

## II. Results and Discussion

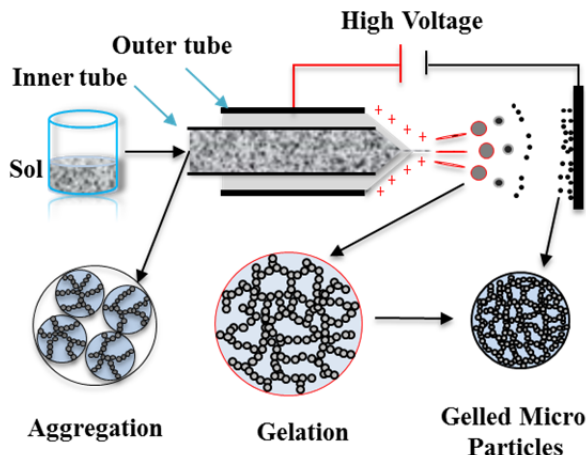
### A. Microspheres Formation

To accomplish the above we employ electrospray as a one-step direct fabrication method. More specifically, electrospray offers a means to create a gel within a droplet by evaporation induced rapid aggregation of nanoparticles containing a small mass fraction of an energetic binder. Figure 1 shows the experimental system.

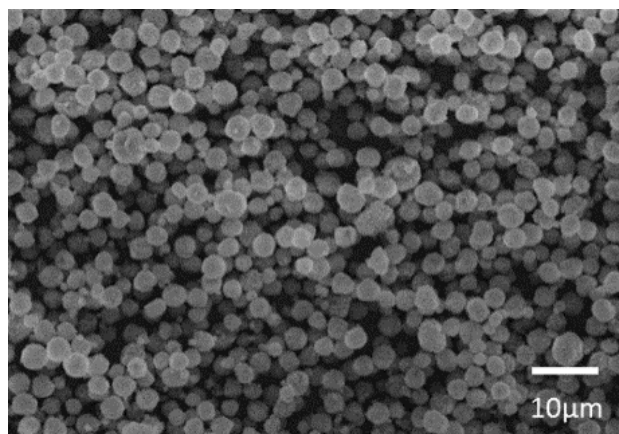
The advantage of electrospray is that electric field induced hydrodynamic instabilities result in jet breakup leading to near uniform droplets whose sizes can be controlled.

### B. Nano Aluminum-Nitrocellulose

To create Al/NC composites we employ ALEX, <50 nm, Argonide Corp which are dispersed into a nitrocellulose polymer solution and electrosprayed to form micro-droplets, which are further dried to form microparticles after solvent removal. In a typical experiment, aluminum nanoparticles were dispersed into a colloidal solution (~17 mg/ml), and then sonicated and stirred to form a suspension. The suspension was then injected by coaxial capillary tubes (the inner diameter of inner tube (22 gauge steel) and the outer tube (17 gauge steel) is 0.41 mm and 1.07 mm, respectively) fed by two syringe pumps and electrosprayed to form gelled aluminum microparticles.



**Figure 1. Schematic showing of electrospray formation of gelled microspheres.**

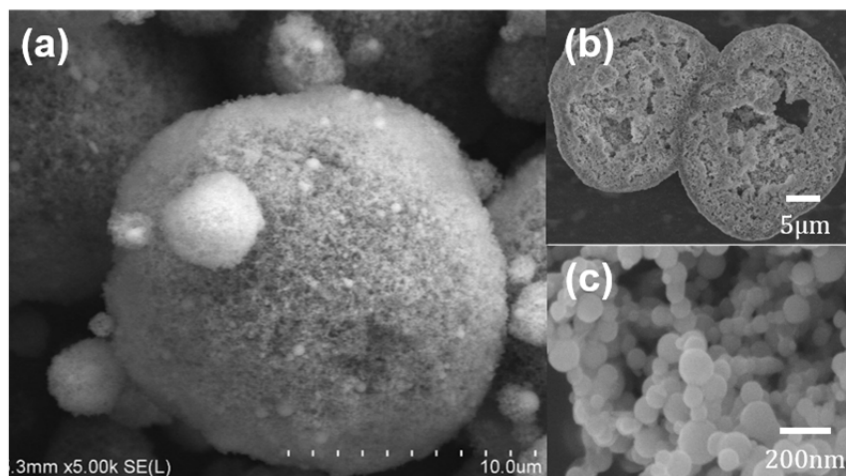


**Figure 2. SEM image of aluminum microspheres produced by electrospraying. (Inner tube flow rate: 0.5ml/h)**

Figure 2 shows scanning electron microscopy (SEM) image of electrosprayed gelled samples. The particles are found to be highly spherical with diameters of several micrometers, which can be varied depending on the Al nanoparticle concentration, and nitrocellulose content.

A close up view in Figure 3a reveals a porous structure of gelled aluminum microparticles with a diameter of ~16  $\mu\text{m}$  (10 wt. % NC). Also seen in Figure 3a are some smaller particles, which can be ascribed to fission of the primary droplets by Coulombic crowding. Cross-section SEM images in Figure 3b and a high resolution SEM image in Figure 3c further reveals the porous structure of the microparticle, which shows that while some cavities exist within the microparticles, for the most part the gel extends throughout the particle. The surface topology at still higher magnification (Figure 3c) shows that the structure has retained the primary particle structure comprising the gel. Brunauer-Emmett-Teller (BET) measurements indicate a surface area of  $20 \text{ m}^2 \text{ g}^{-1}$  for the gelled aluminum microparticles shown in Figure 3a-c, which is close to that for an individual ~50 nm aluminum nanoparticle, implying that the whole microparticle structure is accessible. Thus, on a per unit mass basis the specific surface area of the gelled microparticle is equivalent to the individual primary particles. This latter point is important for the expectation of high or comparable reactivity to the nascent aluminum nanoparticles. On

the other hand one should expect that it is the exposed outer surface of the mesosphere that will have the most impact on the viscous behavior in a formulation. As shown in Figure 1, the chains of NC with nano-Al aggregate in the prepared semi-diluted sol. With the evaporation of solvent within the droplets, the aggregate chains experience crowding and jam against each other to progressively create a three-dimensional porous network, which serves as the main structural skeleton, which is stabilized by the nitrocellulose polymer binder to create the gelled microparticles.

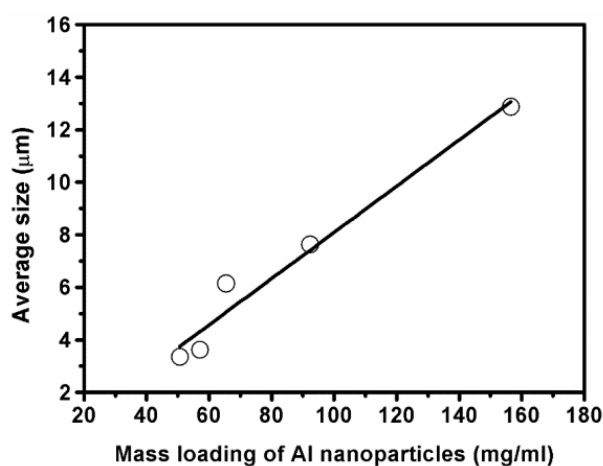


**Figure 3. SEM images of (a) a typical gelled microspheres, (b) cross section, (c) High magnification SEM image of gelled microspheres**

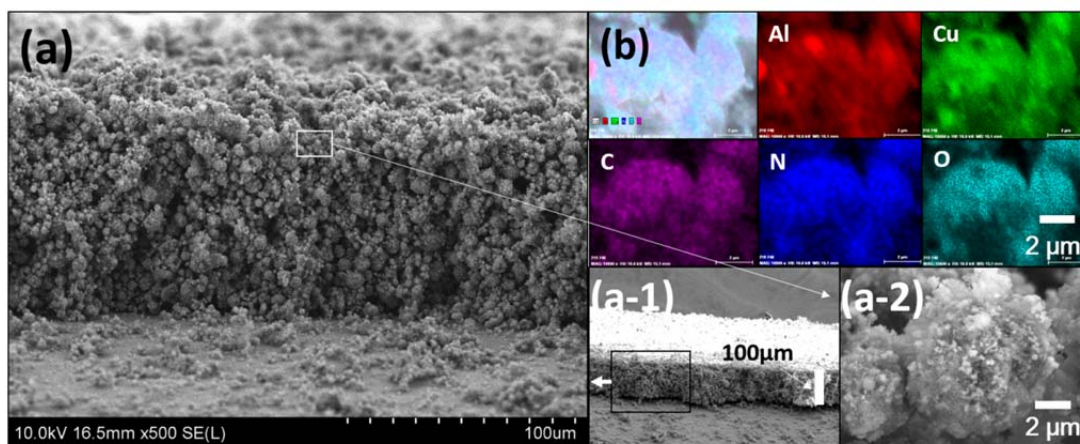
We find that the average size of the gelled microparticles can be systematically changed from 2 μm to 16 μm by increasing the nano-Al particle concentration in the precursor solution, as shown in Figure 4. The fact that the particle size increases so dramatically by changing particle loading implies that larger droplets are being generated by the electrospray, presumably due to the increased precursor solution viscosity rises with increased particle loading.

### C. Nano Aluminum-Copper Oxide-Nitrocellulose

In a similar manner to that for Nano-Al/NC, we can create a thermite mixture with the addition of nanoparticles of copper oxide. In a typical experiment, 180 mg of Al nanoparticles, and 540 mg CuO nanoparticles were dispersed in 0.8 ml ether, and 2.4 ml ethanol, together with 1.4 ml of the collodion solution (10 wt. % NC). The as prepared suspension was sonicated for another 1 hr, and magnetically stirred for 24 hr. A scanning electron microscopy (SEM) image for a typical Al/CuO sample (10 wt. % NC) is shown in Figure 5. Figure 5a shows that the as deposited particles on the sample collector substrate, forming a 100 μm thick layer (Figure 5a-1), with nominal diameters of ~5 μm (Figure 5a-2). Elemental mapping of the individual microparticles, and X-ray energy disperse spectrum (EDS) (Figure 2b) show that Al and CuO are well mixed state between the fuel and oxidizer nanoparticles, and that the NC is distributed homogeneously within the microparticles.



**Figure 4. Average gelled particle size can be systematically increased by adding more nano-Al.**



**Figure 5. SEM images (a), elemental mapping (b) of Al/CuO microparticles produced by a typical electrospray process. (NC: 10 wt. %).**

#### D. Combustion Evaluation

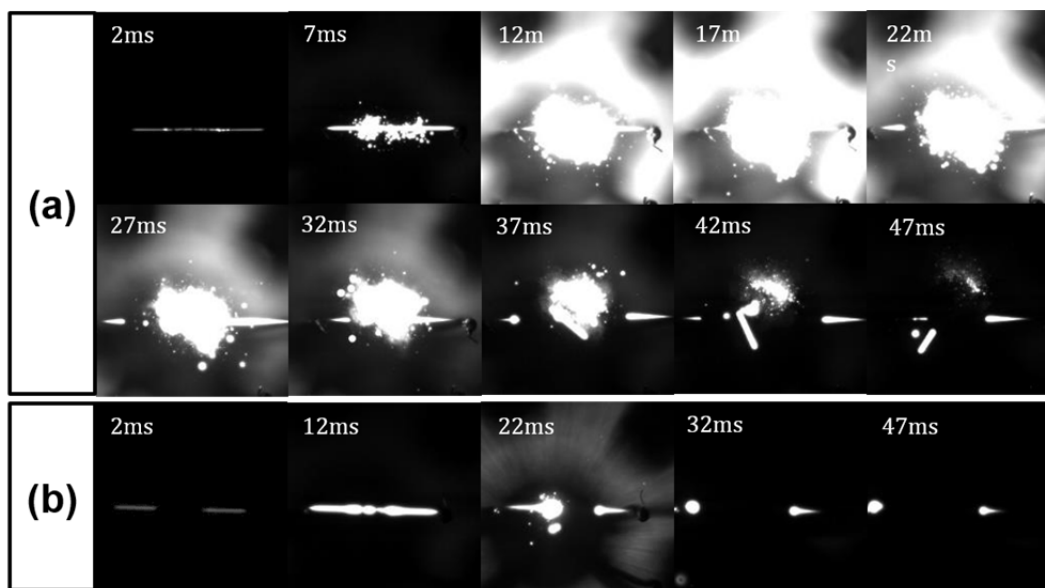
The reactivity of these gelled microparticles was evaluated by coating a thin platinum wire (dia. 76  $\mu\text{m}$ ), which could be rapidly heated to measure the ignition delay time and temperature. The wire was ramped to  $\sim 1600$  K in 3 ms, at a heating rate of  $\sim 4 \times 10^5$  K·s $^{-1}$ . The burning process was recorded by a high-speed camera at the speed of 67000 frames per second to determine the time of sample ignition relative to the heating pulse, and temperature of the wire. For comparison purposes, nano-Al particles, nano-Al mixed with nitrocellulose, as well as microsized aluminum were also tested.

In a second set of experiments the combustion performance of thermite samples was evaluated by igniting 25.0 mg of thermite sample in the combustion cell, instrumented with a fast response pressure transducer and an optical emission sensor. The results for maximum pressure, pressurization rate and burning time as a function of NC content.

In Figure 6a,b and Table 1, the gelled aluminum microsphere (10% NC) showed by far the highest burning duration of  $\sim 64$  ms and the shortest ignition delay time of  $\sim 0.26$  ms, indicating its better combustion performance than nano-Al powder (or nano-Al/NC mixture). The addition of NC serves as both a binder and as an energetic source, which could decrease the ignition delay due to its low decomposition temperature. We attribute the fast reactivity of the gelled material to the localization of the heat release. It is well known that nanoparticles are pyrophoric, but only when in sufficient high concentration. An isolated nanoparticle in air will not burn because of rapid heat loss to the surroundings. The gelled particle is, in effect, an extreme example of this phenomena. The porous nature of the gel enables rapid oxygen transport while the constrained nature of the microspheres constrains the heat released within a small volume, which promotes acceleration of the global reaction. As seen in Table 1, the particles with increased NC have a shorter ignition delay time, but since increasing NC also leads to larger particles we observe an increased burning time.

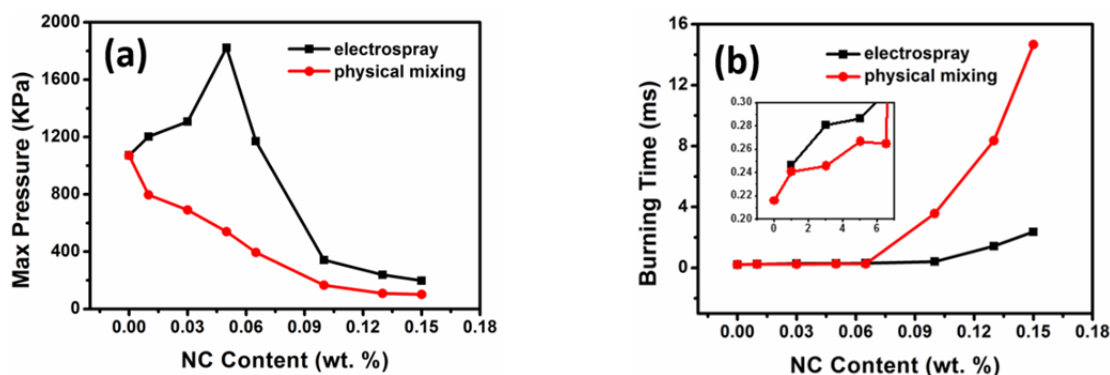
**Table 1. Ignition delay and burn time averaged over three experiments for different formulations.**

Material	Ignition delay time /ms	Burn time /ms
Micron size Al (3.0-4.5 $\mu\text{m}$ )	No ignition	0
Nano Al powder (50 nm)	14.1	14
Mixture of nano Al and NC (10%)	7.2	14
Gelled particles (NC, 1% by mass)	13.2	18
Gelled particles (NC, 3 wt. %, mean size: 2.0 $\mu\text{m}$ )	3.5	46
Gelled particles (NC, 6.5 wt. %, mean size: 3.1 $\mu\text{m}$ )	1.1	56
Gelled particles (NC, 10 wt. %, mean size: 11.1 $\mu\text{m}$ )	0.3	64



**Figure 6. High speed video images: (a): Gelled aluminum microparticles; (b) Nanoaluminum. The labeled numbers are time elapsed after triggering.**

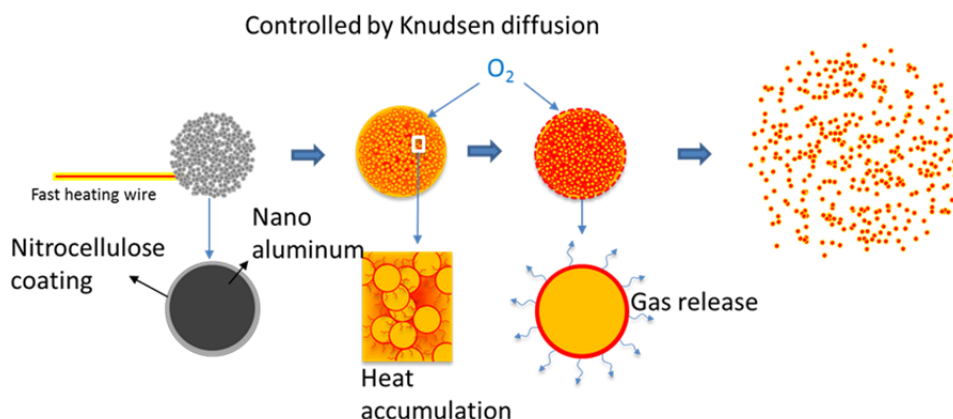
For the case of the Nano Al/CuO/NC system, we find similar behavior with respect to the high speed videography. Shown in Figure 7a are results from pressure cell tests. Both maximum pressure decrease with increasing NC content for Al/CuO nanothermite sample prepared with a conventional physical mixing method. In contrast, for the electrosprayed particles, we find that maximum pressure shows a significant increase with increasing NC content up to 5 wt. %, where the microparticles have maximum pressures of  $\sim 3.4$  larger than the corresponding physically mixed thermite. Above a concentration of 5 wt. %, the electrosprayed microparticles show a rapid decrease on both pressure. Burning times shown in Fig.7c, indicate that NC content has little impact for concentrations below  $\sim 6$  wt. %, but at higher concentrations a significant increase in burning time is observed particularly for the physically mixed sample, which appears to be very sensitive to NC content. Cheetah thermochemical calculation for 25.0 mg Al/CuO/NC in a 13 ml closed cell, shows a monotonic increase in the product pressure with NC content, and thus does not capture the features observed experimentally.



**Figure 7. Pressure cell tests for thermite mixtures a) Maximum pressure; and (b) burning time of the nanothermite samples prepared by electrospray and physical mixing.**

It is widely accepted that the interfacial contact between the fuel and oxidizer plays an important role in the combustion performance of composite energetic materials e.g. nanothermites. The enhanced combustion performance of the electrosprayed microparticles relative to the physically mixed material are suggestive of superior intermixing of the two components and possibly heat transfer related effects.

We propose the following conceptual mechanism of this enhanced burning as illustrated in Figure 8. With nitrocellulose's low decomposition temperature (170 °C) we expect gas generation to occur early during the heating process and combustion to commence with the oxygen within the porous structure. Unlike isolated nanoparticles undergoing oxidation that have high heat loss to the surrounding, rapid reaction within the gelled microsphere should be self-accelerating, because the heat of reaction is trapped within the microsphere, resulting in cooperative heating. Eventually it is also possible that this rapid accumulation of heat and increasing rapid reaction lead to sufficient gas generation so as to overpressure the structural integrity of the gel, and shatter it into isolated burning nanoparticles as evidenced by the large fire ball seen in Figure 6a.



**Figure 8. Proposed combustion process of gelled Al micro particles.**

Similar consideration can be applied to the thermite case as well. At low NC content performance is increased, possibly due to the presence of a ready source of low temperature energetic, generating gas so as to prevent sintering. At higher loading, performance degrades because energy content is degrading, and possibly that we have reached a limit where too much gas generation only serves to dissipate the reactant from each other resulting in reaction quenching.

This latter explanation is consistent with our observation and explanation that localization of the heat release explains the superior reactivity of gelled Al microspheres. The porous microparticles could accumulate the heat within the microstructure while promoting the mass transport at the same time. Instead of isolated or aggregated Al and CuO nanoparticles undergoing redox reaction with high heat loss to the surrounding, the microparticle may serve to accumulate some of the heat of reaction leading to a self-accelerating behavior. At some point adding additional NC (> 6.5 wt. %,) apparently offers diminishing returns, by overpressuring the structural integrity of the microparticle and leading to its disintegration into smaller structures. At this point both pressure and pressurization rate drops sharply from the peak value to less than 400 KPa and 0.5 KPa/ $\mu$ s, respectively (from 5 wt. % to 10 wt. %). In fact, this also increases the burning time of the nanothermite microparticles, as shown in Fig.7c.

### III. Conclusions

In summary, gelled aluminum and thermite microspheres with a narrow size distribution were synthesized by a one-step electrospray method. The microstructures of the composite particles reveal a porous gelled inner structure with nano features. We show that the average microsphere size can be tuned over a relatively large range. Most interesting however is that these gelled microspheres show superior reactivity, than the nascent nanoparticle comprising the gelled particle. We expect that the unique gelled microsphere structure with nano building blocks could potentially circumvent the problems associated with trying to utilize nanometals in propellants.

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